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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the preparation of 2,4,6-Trialkylated Phenols

We, N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

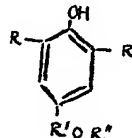
This invention relates to a novel process for the preparation of 2,6-dialkyl para-alkyl phenols.

Previously numerous methods and techniques have been described for the preparation of such alkylated phenols. The purpose of these numerous teachings has been to achieve more efficient yields of desired products, for it invariably happens that in the preparation of alkylated phenols mixed products are produced. This has the disadvantage that additional processing steps are required to separate the mixture of alkylated phenols. Furthermore, it often happens that yields of the desired product are too low. Another disadvantage of prior art methods is that the starting materials are usually para-monoalkylphenols such as cresol. Not only are such starting materials costly but the available supply is limited and uncertain since it is most commonly obtained from petroleum refining processes. Furthermore, the prior art processes for the preparation of the para-alkyl derivatives of 2,6-dialkyl phenols often involve the reaction of para-alkylphenols with an olefin, such as isobutylene, in the presence of acidic materials. This has the further disadvantage that the olefin is polymerised to a certain extent thus reducing the yield and contaminating the desired product. It is an important advantage of this invention that para-alkylphenols are not used in the processes thus eliminating the necessity for the use of those costly materials and at the same time assuring an abundant supply of starting materials in the form of phenol and

olefins. It is an equally important advantage of this invention that polymers are not produced during the process of this invention thus avoiding the waste attendant with prior art methods. By the present invention, it is found that alkylated phenols are prepared by novel processes which are totally unexpected in view of the prior art.

The invention is, accordingly, a process for the preparation of a 2,6-dialkyl para-alkyl phenol in which in a first stage, a 2,6-dialkyl phenol is reacted with an acyclic saturated aldehyde having from 1 to 8 carbon atoms in the molecule in the presence of an acyclic and saturated alcohol having not more than 6 carbon atoms in the molecule and an alkaline metal hydroxide the reaction mixture having a pH greater than 7.0, after which, in a second stage, the 4-alkoxyalkyl 2,6-dialkyl phenol thus formed is hydrogenolized in the presence of a hydrogenation catalyst.

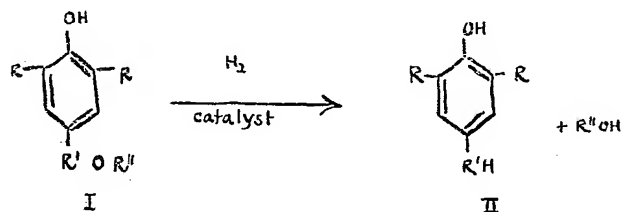
In the first stage a compound of the general formula



is formed in which R, and R¹¹ are alkyl radicals, and R¹ is an alkylene radical.

The alkyl radicals, indicated by R in the above formula may have up to 8 carbon atoms or more. The alkylene radical indicated by R¹ has from 1 to 8 carbon atoms, whilst the alkyl radical indicated by R¹¹ has not more than six carbon atoms.

In the second stage the 4-alkoxy alkyl 2,6-dialkyl phenol is treated with hydrogen at an elevated temperature and pressure in the presence of a hydrogenation catalyst. This reaction may be represented by the following equation:—



In the novel process of this invention, the starting material is any 2,6-dialkylphenol, which may be prepared by any convenient means. One such means is by the reaction of phenol with about two moles of an olefin in the presence of certain organo-aluminium compounds. Typical olefins which add to the 2,6-position of phenol as indicated above, include propylene, butylene, isobutylene, pentene-1, pentene-2, hexene-3 and octene-4. Actually, the method used to alkylate phenol in the 2,6-position is immaterial as long as the starting material used in the present process is blocked in the ortho-positions. By this means, the ether is formed in the 4-position as shown by Formula I. Therefore, in the above formula, the R's may be the same or different alkyl radicals.

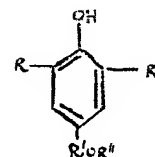
It is surprising that in the process according to the present invention the treatment with hydrogen cleaves the ether because it is known that when 2,6-diisopropylphenol and 2,6-di-tert-butylphenol are subjected to catalytic hydrogenation 2,6-diisopropylcyclohexanol and 2,6-di-tert-butylcyclohexanol, respectively, are produced. Thus, it is to be expected that when the benzyl ether is treated with hydrogen the ring would become saturated. Instead the ring remains unaffected.

The aldehyde which is used in the formation of the ether is selected from those aldehydes which are acyclic and saturated. Aldehydes of this type having not more than 8 carbon atoms are being used since aldehydes having a greater number of carbon atoms are found to react only with considerable difficulty. It is preferred that the aldehyde has not more than 4 carbon atoms and the most preferred species is formaldehyde or a compound forming formaldehyde under the reaction conditions as this aldehyde reacts more easily and ultimately gives products which are very useful as anti-oxidants.

The alcohol used is any acyclic and saturated alcohol having not more than 6 carbon atoms. In actual practice it is preferred that methanol is used as other alcohols are found to produce substantially lower yields. Further, as the alkyl radical of the alcohol is subsequently cleaved in the hydrogenolysis, no practical advantage accrues from using alcohols other than methanol. It will be understood, however, that the invention is not limited to methanol and alcohols such as ethanol, propanol, isopropanol and butanol may be used although they are less satisfactory. The basic

component of the reaction mixture must be an alkaline metal hydroxide, for example, sodium hydroxide or potassium hydroxide.

As indicated above, when a 2,6-dialkylphenol is reacted with an aldehyde in the presence of an alcoholic base, a benzyl ether, which may be represented by the following, is formed



The R's are the same or different alkyl radicals, R¹ is an alkylene radical having from 1 to 8 carbon atoms, and R¹¹ is an alkyl radical derived from the alcohol. In the preferred embodiment the R's have up to 6 carbon atoms and in the most preferred embodiment the R's are tertiary-butyl, R¹ is methylene, (derived from formaldehyde), and R¹¹ is -CH₃ (derived from methanol).

The conditions of reaction for the preparation of the ether are found to be quite variable but certain preferences are made in order to obtain the most beneficial results. In general an excess of the starting 2,6-dialkylphenol in relation to the other reactants is undesirable as such an excess favours the formation of unwanted bisphenols as by-products. Thus, for each mole of the 2,6-dialkylphenol a quantity of an aldehyde (for example as 37% aqueous formaldehyde), in the range of 1.05 to 7 moles may be used, about 2.5 to 5 moles being preferred. The alcohol and aldehyde are present in excess as it is found that this represses the formation of bis-phenols. On the other hand, it is a disadvantage to use too great an excess of either as the excess must eventually be removed at later stages of the process.

The process is fully operable if the alcohol is present in about stoichiometric amount but this is not desirable. As a generalisation it may be stated that the alcohol is preferably present in amounts ranging from about 5 to 30 moles with about 7 to 25 moles being more preferred.

The quantity of the alkaline metal hydroxide may be varied over a wide range but it should be present in an amount at least sufficient to give the reaction mixture a pH greater than 7.0. In the preferred embodiment it is desirable to use sufficient alkaline metal

hydroxide to bring the reaction mixture to a pH of between about 9 and 12. The use of a pH substantially below about 9.0 but greater than 7.0, causes considerably longer reaction times whereas a pH substantially in excess of 12 increases the yield of by-products.

The temperatures used in the preparation of the ether may vary from about 35°C to about 100°C, and even higher, but temperatures between 35°C and 75°C are preferred. Temperatures which are substantially higher than 100°C result in reduced yields of the ether and corresponding increases in the amount of by-product. Further, at the higher tempera-

tures, a Cannizzaro reaction may occur with formaldehyde, and similar aldehydes which have no active hydrogen in the alpha-position to the carbonyl group, with the formation of a formic acid salt. The time required for the reaction to be completed will vary with a number of factors such as the ratio of the reactants used, the temperature of the reaction and the pH. The effect of reaction time is generally shown by Table I where 2 moles of 2,6-ditert-butyl-phenol, 15 moles of methanol, 0.66 mole of water and 2.1 moles of formaldehyde (as 37% formalin) were reacted at 40 to 45°C with 8 grams of sodium hydroxide.

TABLE I

Hours Reacted	Composition of Product %m		
	Methoxymethyl-2,6-di-tert-butylphenol (Ether)	By-product ^{a)} Bisphenol	2,6-Di-tert-butylphenol
1	26	3	71
3	50	6	44
5	63	12	25
6.5	65	16	19

a) 4,4'-Methylene bis(2,6-di-tert-butylphenol).

The fact that the ethers are easily formed by merely reacting the several ingredients for the desired period of time, and that this reaction is capable of wide variation is an advantage. Some variations are found to be extremely beneficial, for example, if desired, paraform may be used with considerable advantage instead of formalin. In order for the paraform to go into solution the pH of the reaction mixture must be held fairly high.

The separation of the by-product need not be undertaken prior to the hydrogenolysis since the by-product is not ordinarily effected thereby. If desired, however, the reaction product obtained as in the following examples may be treated to remove the by-product. This may be accomplished by simple distillation at reduced pressures in the order of 1 to 5 mm, or more, at temperatures ranging from about 100°C to 175°C. After the etherification is complete, it is most desirable to immediately proceed with the hydrogenolysis step without separating the by-product as it is found that the ether on standing in the alkaline medium slowly reacts with unreacted 2,6 dialkyl-phenol to increase the quantity of the by-product.

The hydrogenolysis may be conducted in a liquid phase using any non-reactive solvent such as lower alcohols containing between one and eight carbon atoms per molecule, n-alkanes and aromatic hydrocarbons, or, if desired, no solvent need be used. Hydrogenolysis is found to proceed rapidly at tem-

peratures of 110°C to 170°C and pressures of 100 to 700 psig, or higher, wherein a substantial portion of the pressure may be due to the partial pressure of the solvent. Still higher pressures may be used without adversely effecting the hydrogenolysis but temperatures in excess of 250°C should not be used as the alkyl groups in the 2,6-position will be stripped. In one experiment temperatures in the order of 200°C and pressures of about 2000 psig were used without substantially effecting the yield.

The hydrogenolysis requires the use of a suitable hydrogenation catalyst. Such catalysts are preferably selected from metals of Groups I, II, IV, V, VI, VII and VIII of the Periodic Table, their alloys and derivatives such as their sulphides, oxides and chromites. Examples include silver, copper, iron, manganese, molybdenum, platinum, chromium, cobalt, rhodium, tungsten, mixtures of metals, such as copper-silver mixtures, copper-chromium mixtures, nickel-cobalt mixtures, and their derivatives such as copper oxide, copper chromite, nickel sulphide and silver sulphide. Especially preferred catalysts are the members of the group consisting of nickel, copper, cobalt, iron, chromium, silver and platinum, and their oxides, sulphides and chromites. In particular copper chromite turned out to be a suitable catalyst. These catalysts may be employed in a finely divided form and dispersed in and throughout the reaction mixture, or they may be employed in a more massive state, either in

the essentially pure state or supported upon, or carried by, an inert carrier material such as pumice, kieselguhr, diatomaceous earth, clay, alumina, charcoal or carbon, the reaction mixture being contacted with the catalyst by flowing the mixture over or through a bed of the catalyst, or according to other methods known in the art.

The amount of the catalyst employed may vary over a considerable range depending upon such factors as the type of catalyst employed, the specific ether and the temperatures and pressures used. In general, the amount of the catalyst ranges from about 0.1% to 35% by weight of the ether, amounts ranging from about 1% to 15% being preferred. Depending on the several variables involved, it will be found that the catalyst may be recovered and reused for several batches before it becomes necessary to recharge and/or replace it.

The hydrogenolysis may be conducted in any suitable apparatus of the type that is conventionally employed for hydrogenation processes. Thus, for example, the ether, catalyst and solvent, can be charged to a pressure-resistant vessel equipped with the necessary inlets and outlets, heating means, pressure gauge and thermometer. After the hydrogenolysis is complete, the reaction product is separated from the by-product whereupon it is found that the ether has been substantially completely converted to the desired alkylated phenol.

EXAMPLE I

First Stage : Run 1

1 mole of 2,6-di-tert-butylphenol, 1.06 moles of formaldehyde as 37% formalin, 7.5 moles of methanol, 0.66 mole water (excluding the water in the formalin) and sufficient sodium hydroxide to raise the pH to 9.0 were charged to a reaction vessel equipped with an agitator, thermometer reflux condenser and heating and cooling means. The temperature was raised to 45°C and maintained within the range of 40 to 49°C for 60 minutes. By flashing the reaction product in a Claisen distillation column at about 140°C at 4 mm. mercury 26% of 4-methoxymethyl-2,6-di-tert-butylphenol was recovered, which was about a 29% conversion of the phenol. The by-product amounted to about 3 mole-percent of the reaction product. By reacting the same mixture for 6½ hours, 65 mole-percent of the ether was obtained which amounts to an 81 molar-percent conversion of the starting phenol. There was, however, 16 mole-percent of by-product formed.

First Stage : Run 2

The procedure of Run 1 was repeated using 10 moles of methanol and 0.95 mole of water. After reacting for 2½ hours 0.75 mole of the ether separated out, based on an 80% conversion of the starting phenol. The by-product

amounted to about 20% of the completed reaction mixture.

First Stage : Run 3

The procedure of Run 1 was repeated except that the reaction was conducted at about 72°C for 30 minutes. The reaction product contained about 64% of the ether and about 25% of by-product, the remainder being unreacted phenol.

First Stage : Run 4

The procedure of Run 1 was repeated using 5.0 moles of formaldehyde, as 37% formalin, and 25 moles of 75% methanol. The reaction product contained 74% of the ether and 5% of by-product after reacting for 4 hours at 45 to 47°C. Reacting for 10 hours gave a reaction product containing 91% of ether and 7% by-product, the balance being unreacted 2,6-di-tert-butylphenol.

First Stage : Run 5

0.5 Mole of 2,6-di-tert-butylphenol, 2.5 moles of paraform, 12.5 moles of methanol, 0.05 mole of sodium hydroxide and 68 moles of water were charged to a reaction vessel equipped as in Run 1. After reacting for 1½ hours at 70°C a reaction mixture was obtained having about 92% 4-methoxymethyl-2,6-di-tert-butylphenol and about 8% by-product. Lesser yields of the ether were obtained using small amounts of paraform with a corresponding increase in the by-product.

Second Stage : Run 1

150 Grams of 4-methoxy-methyl-2,6-di-tert-butylphenol, 45 grams of copper chromite, and a small amount of methanol were added to a hydrogenation vessel equipped with suitable inlets, thermometer, and heating and cooling means. The vessel was filled with hydrogen to a pressure of 500 p.s.i.g. and the temperature is raised to and maintained at 130 to 145°C. After about 30 minutes the hydrogenolysis was complete and the contents of the vessel were removed and separated whereupon it was found that substantially 100% conversion of the ether has taken place to yield 2,6-di-tert-butyl-p-cresol.

Second Stage : Run 2

The procedure of Run 1 in the second stage was repeated except that the quantity of the catalyst was reduced to 3 grams. Substantially the same result was obtained. The catalyst was recovered and reused in subsequent runs.

EXAMPLE II

First Stage

The procedure of Run 1, first stage of Example I was repeated using 2,6-diisopropylphenol, formalin and ethanolic base. The reaction product contained 4-ethoxymethyl-2,6-diisopropylphenol, the by-product 4,4'-methy-

lene bis(2,6-diisopropylphenol) and a considerable amount of the unreacted starting phenol.

Second Stage : Run 1

- 5 The ether prepared by the procedure of the first stage was hydrogenolysed by the procedure of Run 1 of the second stage of Example I to yield 2,6-diisopropyl-p-cresol.

Second Stage : Run 2

- 10 In the same manner as in Run 1 of the second stage of Example I, 4-ethoxymethyl-2,6-di-tert-butylphenol was treated with hydrogen using 3000 p.s.i. of hydrogen pressure. The hydrogenolysis was found to be complete in several minutes.

15 EXAMPLE III

First Stage

- 20 The procedure of Run 1, first stage of Example I was repeated using equimolar amounts of acetaldehyde. The reaction product contained considerably lesser amounts of the ether 4 - (1-methoxyethyl)-2,6-di-tert-butylphenol. The bulk of the reaction product was the unreacted phenol.

Second Stage

- 25 The procedure of Run 1 in the second stage of Example I was repeated and the ether was converted to 4-ethyl-2,6-di-tert-butyl phenol.

EXAMPLE IV

First Stage

- 30 Using the same procedure as in the preceding examples, butanol was used in the preparation of the alcoholic base, resulting in the formation of the corresponding ethers. In other runs, propionaldehyde and n-capro-aldehyde were used instead of formaldehyde.

Second Stage

- 40 The procedure of Run 1 in the second stage of Example I was repeated and the ethers converted to the corresponding trialkylated phenols.

It will be apparent that the hydrogenolysis will require longer reaction times at lower temperatures and pressures.

WHAT WE CLAIM IS:—

- 45 1. A process for the preparation of a 2,6-dialkyl para-alkyl phenol in which in a first stage, a 2,6-di-alkyl phenol is reacted with an acyclic saturated aldehyde having from 1 to 8 carbon atoms in the molecule in the presence of an acyclic and saturated alcohol having not more than 6 carbon atoms in the molecule and an alkaline metal hydroxide in a reaction mixture having a pH greater than 7.0, after which, in a second stage, the 4-alkoxyalkyl 2,6-dialkyl-phenol thus formed is hydrogenolysed in the

presence of a hydrogenation catalyst.

2. A process according to claim 1, in which in the first stage from 1.05 to 7 moles of aldehyde per mole of 2,6-dialkyl phenol are used.

3. A process according to the preceding claim in which in the first stage from 2.5 to 5.0 moles of aldehyde per mole of 2,6-dialkylphenol are used.

4. A process according to any one of the preceding claims in which in the first stage from 5 to 30 moles of alcohol per mole of 2,6-dialkylphenol are used.

5. A process according to the preceding claim in which in the first stage from 7 to 25 moles of alcohol per mole of 2,6-dialkylphenol are used.

6. A process according to any one of the preceding claims, in which during the first stage the reaction mixture is maintained at a pH within the range of 9 to 12.

7. A process according to any one of the preceding claims, in which during the first stage the reaction temperature is kept between 35°C and 100°C.

8. A process according to the preceding claim, in which during the first stage the reaction temperature is kept between 35°C and 75°C.

9. A process according to any one of the preceding claims, in which the aldehyde used in the first stage is formaldehyde or a compound forming formaldehyde under the reaction conditions.

10. A process according to any one of the preceding claims, in which the alcohol used in the first stage is methanol.

11. A process according to any one of the preceding claims, in which the 2,6-dialkylphenol used as starting material in the first stage is 2,6-di(tert. butyl)phenol.

12. A process according to any one of the preceding claims, in which the second (hydrogenolysis) stage is carried out at a temperature between 110° and 170°C. and at a pressure between 100 and 700 psig.

13. A process according to any one of the preceding claims, in which in the second stage copper chromite is used as a hydrogenation catalyst.

14. Processes for the preparation of 2,6-dialkyl paraalkyl phenol in accordance with claim 1 substantially as hereinbefore described with special reference to the Examples.

15. 2,6-dialkyl para-alkyl phenols whenever prepared according to any one of the preceding claims.

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